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CENTRIFUGAL CASTING OF METALS AND CERAMICS USING THERMIT REACTIONS

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Abstract : Ceramic linings for metal pipes and shaped castings of metals and alloys are produced by carrying out thermit reactions under the influence of centrifugal force. The adiabatic temperature, self propagation and the combustion velocity of the thermit reaction are effected when the reaction is diluted with the product phases. The dilution has profound effect on these properties of the reaction when the ceramic product phase of the reaction is used as inert diluent.

Keywords : ceramics, centrifugal casting, thermit reactions

1. INTRODUCTION

Many solid-solid chemical reactions are accompanied by the evolution of heat. If such a solid-solid chemical reaction is sufficiently exothermic, then a mixture of powdered reactants, either in a crucible or formed into a free-standing shape, may be ignited by a hot thermal source. From the point of ignition, a combustion wave rapidly self propagates through the reactants, converting them to product(s). During such reactions, high temperatures (1000 to 4000K) are generated at the combustion front. The speed of reaction is relatively fast with combustion wave velocities varying from 0.1 to 10 $cm.s^{-1}$. Such reactions are also accompanied by high rates of heating (upto 10^6 $deg.s^{-1}$) and high thermal gradients (upto 10^7 $deg.cm^{-1}$) at the combustion front. Due to high temperatures at the combustion front, impurities in the reactant powders are sometimes volatised in a manner similar to zone refining. This can result in the production of product(s) with better purity.

The method to use such highly exothermic reactions for the synthesis of materials is commonly referred to as the Self propagating High temperature Synthesis (SHS) method. This acronym was first proposed by Russian scientists although several other terminologies like combustion synthesis, gasless combustion, self propagating combustion and self propagating exothermic reactions are also used to describe the same method. Such a method was first utilised by Goldschmidt in 1895 to produce metals and alloys from their respective oxides using aluminium as the reducing agent. The word thermit was first coined by Goldschmidt in 1908 to describe such exothermic reactions. Currently the term Thermit reaction is used to describe a much broader class of reactions and can be defined as an exothermic reaction which involves a metal reacting with a metallic or a non metallic oxide to form a more stable oxide and the corresponding metal or non metal of the reacting oxide. This is a form of oxidation-reduction reaction which can be written in a general form as

$$M + AO \rightarrow MO + A + \Delta H$$

where M is a metal or an alloy and A is either a metal or a nonmetal, MO and AO are their corresponding oxides, and ΔH is the heat generated by the reaction. This type of reaction is characterised by a large heat release which is often sufficient to heat the product phases above their melting points. Because of the large oxothermic heat, a thermit reaction can generally be initiated locally and can become self sustaining. This makes

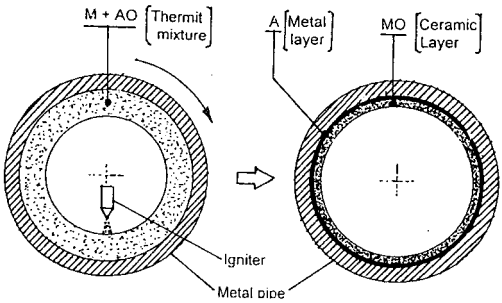

Fig. 1. Schematic representation of the method for providing ceramic linings to metal pipes.

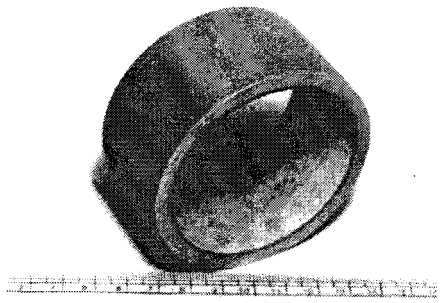

Fig. 2. Ceramic lined metal pipe produced under a centrifugal force of 250G

their use extremely energy efficient. The fact that many thermit reactions yield molten products that consist of a heavier metallic phase and a lighter oxide phase which can be separated by gravity, makes these reactions potentially useful in a variety of metallurgical applications[1-6]. The process of separation can be accelerated by the use of centrifugal force. Based on this principle, Odawara and his co-workers in Japan developed a centrifugal method to provide ceramic linings for metal tubes[7-10]. A.G.Merzanov and his co-workers of Russia utilised such reactions for the synthesis of many refractory inorganic materials such as carbides, borides, silicides and their combinations[11]. More recently, thermit reactions have become important in the synthesis of refractory ceramic and composite materials[12-16].

This paper describes briefly the methods developed in our laboratory to (a) provide ceramic linings for metal pipes and (b) produce shaped castings from metals and alloys using such reactions. The effects of dilution on such reactions are also discussed.

1.1 Ceramic lining for metal pipes

Many industrial applications require metal pipes and vessels with wear, corrosion and heat resistant ceramic linings. A method is developed in our laboratory to provide ceramic linings to such axisymmetric metal pipes and vessels to meet these requirements. This is similar to the centrifugal thermit process developed by the Japanese researchers[7]. This method, which provides a rapid and economical method for producing such metal-ceramic composite pipes, is illustrated in Fig.1. It involves first packing a powdery thermit mixture, consisting of a reducible metal oxide and a strongly reductive element, against the inner surface of the pipe and then igniting the mixture at one point while the pipe is being rotated about its central axis. Once ignited, the reaction proceeds first along the inner surface of the thermit mixture, packed inside the metal pipe, and subsequently in the radial direction simultaneously[7]. Because of the large amount of heat released by the thermit reaction, the product phases, namely ceramic and metal, are in the liquid state. They will undergo separation due to the difference in their densities. The centrifugal force accelerates the process of their separation and the effective expulsion of trapped and impurity gases. After solidification and cooling, this results in the formation of low porosity ceramic layer over the high density metal layer. The metal layer, which forms the intermediate layer, is bonded to the inside of the metal pipe.

A steel pipe of 68 mm inside diameter and 5mm wall thickness which is lined with 1.25 mm thick alumina based ceramic by this method, using the thermit reaction $Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe$ is shown in Fig. 2. The cross sectional microstructure of the pipe is shown in Fig.3. The iron layer, which binds the ceramic layer to the pipe, is observed to have metallurgical bond with the steel pipe by fusion. However, the bond between the

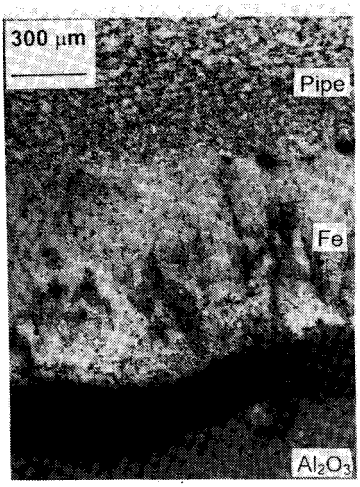

Fig. 3. Sectional microstructure of the ceramic lined steel pipe

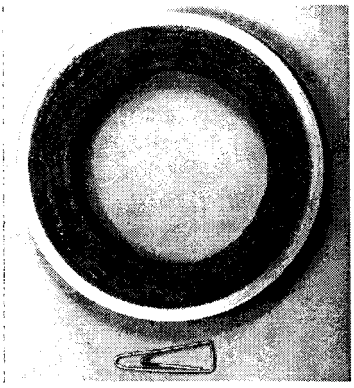

Fig. 4. Multilayered ceramic lined steel pipe produced under a centrifugal force of 200G

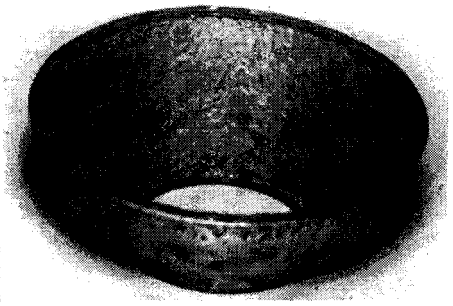

Fig. 5. Ceramic lined conical steel part.

solidified layers of iron and ceramic is believed to be predominently mechanical as the two layers are found separated at the interphase. This mechanical bond is believed to be due to the irregularities present on the surfaces of the metal and ceramic layers at the interphase. The difference in the solidification shrinkages of the product phases and the difference in their coefficients of thermal expansion are believed to have caused the separation of the two layers at the interphase after solidification and cooling.

This method is recently extended to provide multilayered ceramic linings to metal pipes. One such 20mm long steel pipe with 69mm inside diameter and 3mm wall thickness lined with four layers, each layer with 2mm thickness, of alumina based ceramic is shown in Fig. 4. The method is also recently modified to provide single or multilayered ceramic linings for conical metal components[17]. Fig. 5 shows a truncated conical steel part, having 100mm maximum diameter, 40mm length, 60^{o} apex angle and 2mm wall thickness, lined with 1.5 mm thick alumina based ceramic using this method.

1.2 Centrifugal casting of shaped components

Many commercially adopted casting methods, such as sand casting, investment casting, die casting and centrifugal casting are useful to produce shaped castings from metals and alloys. These methods require a suitable furnace to produce molten material which is subsequently poured or forced into the cavity of a metal or refractory mould to produce a shaped casting. Thus, these methods consume more power and require separate steps of melting and casting. A method is developed in our laboratory for producing such shaped components by centrifugal force using thermit reactions[18]. This is a one step process which requires no external heating source to produce molten material for casting. This method is illustrated in Fig. 6. A refractory mould(2) is fitted to one end of a hollow refractory container(1) such that the passages provided in the mould for the flow of molten material are open to the hollow space of the refractory container. The refractory container is closed at this end by a refractory plate(3). The refractory container, along with the

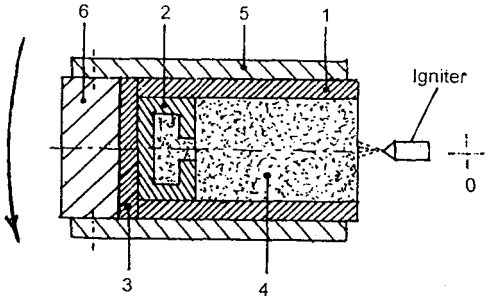

Fig. 6. Schematic representation of the method for producing shaped castings of metals and alloys.

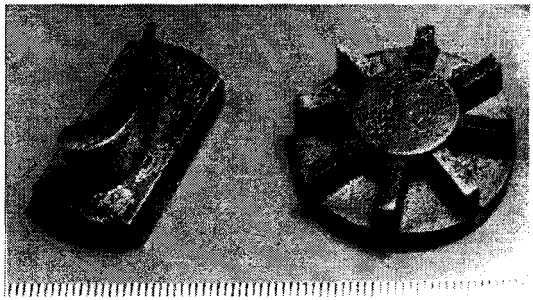

Fig. 7. Shaped castings of nickel aluminide produced under a centrifugal force of 450G

mould and refractory plate, is encapsulated in a metal pipe(5). The metal pipe is closed at the end where the refractory mould is housed by a metal plate(6). The refractory container is filled with the desired thermit mixture(4) comprising of a reducible metal oxide and a strongly reductive element. The whole assembly is rotated about an external axis O. The thermit mixture in the refractory container is ignited at least at one point on its free surface to initiate the thermit reaction. The reaction then propagates through the remaining thermit mixture in the refractory container. The strongly reductive element oxidises to molten metal oxide and the reducible metal oxide reduces to molten metal. Because of the differing densities, the molten metal gets separated rapidly from the molten metal oxide by centrifugal force and fills the cavity of the mould. The molten metal oxide collects outside the mould in the hollow space of the refractory container. After solidification and cooling, the mould, containing the shaped casting, and the solidified metal oxide are removed from the refractory container. The metal oxide is separated from the mould and the mould is destroyed to get the shaped casting of the desired metal. Suitable alloying elements can be blended with the initial thermit mixture to get the desired shaped casting from the required alloy using this method. Two shaped components of nickel aluminide produced by this method are shown in Fig. 7.

1.3 The effects of dilution on the thermit reactions

Many combinations comprising of the strongly reducing element and the reducible metal oxide, conventionally used in thermit reactions, may be used in the methods (a) and (b) described earlier. The strongly reducing element can be selected from the group consisting of aluminium, magnesium and silicon. However, aluminium, having an ignition temperature of about 1500K, is the most preferred reducing element owing to its lower melting point, higher boiling point, lower vapour pressure, good reducing potential, oxide having lower melting point, low cost and easy availability. On the other hand, the thermit reaction with magnesium alone as the strongly reducing element is too violent and hence is less preferred while the ignition temperature of silicon alone is too high. However, the use of these elements in combination is useful for controlling the ignition temperature and producing ceramic lining from the combination of different oxides. The reducible metal oxides can be chosen from the oxides of iron, nickel, copper, tungsten, molybdenum, vanadium, chromium, titanium, magnesium etc.

The heat released by such a thermit reaction heats up the product phases. The maximum temperature to which the products are raised as a result of this exothermic reaction is called the adiabatic temperature, T_{ad}. This temperature can be estimated from the enthalpy, H, of the reaction and the heat capacities, C_p, of the product phases, assuming

Table I. Reaction enthalpies (ΔH), adiabatic temperatures (T_{ad}) and melting and boiling points (T_m and T_b respectively) of product metals

	Reaction	ΔH (kJ)	T_{ad} (K)	T_m (K)*	T_b (K)*
1	$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$	856	3133	1809	3133
2	$3NiO + 2Al \rightarrow Al_2O_3 + 3Ni$	956	3188	1728	3188
3	$3CuO + 2Al \rightarrow Al_2O_3 + 3Cu$	1212	2833	1358	2833
4	$Fe_2O_3 + 3Mg \rightarrow 3MgO + 2Fe$	323	3076	1809	3133
5	$2Fe_2O_3 + 3Si \rightarrow 3SiO_2 + 4Fe$	311	2626	1809	3133

* from Ref. 22

that the reaction takes place under adiabatic conditions, from the following heat balance equation[19,20]

$$\Delta H = \int_{T_a}^{T_{ad}} C_p dT \tag{1}$$

where T_a is the ambient temperature. The T_{ad} provides not only a quantitative measure of the exothermicity of the reaction, but also a quick determination of the ability of the reaction to self propagate. As a rule, the reaction can self propagate if T_{ad} exceeds 2000K[20]. Moreover, the information of T_{ad} also provides some insight to the possible states of the reactants during interaction, whether in solid, liquid, gas or a combination of these.

A few thermit reactions, useful for the methods (a) and (b), and their estimated H and T_{ad} are shown in Table I. In these reactions, T_{ad}, which is the maximum temperature reached during the reaction, exceed the melting points of the product phases. This condition is to be necessarily met by any thermit reaction if it has to be used in the methods (a) and (b), described earlier, as separation of the product phases take place in these methods while the product phases are in liquid states. In some thermit reactions, the T_{ad} is the boiling temperatures of their product phases which have lower boiling points compared to their coproduct phases, as in reactions 1,2 and 3 in Table I. In such cases, the lowering of T_{ad} help in overcoming the vaporisation losses of these product phases. The lowering of T_{ad} also brings about changes in the states of the reactants during their interactions when these reactions take place. The T_{ad} of these reactions can be lowered by adding inert diluents to their initial thermit mixtures[21]. If one of the products of the thermit reactions is itself used as an inert diluent, then more quantity of that product phase, in molten state, can be produced. This helps to produce a thicker ceramic lining by method (a) or a larger shaped casting by method (b) using the same quantity of the undiluted thermit mixture. These effects of inert diluents are explained in the following using thermit reaction 2 of Table I as an example.

Assuming that the inert diluents do not take part in the chemical reaction, this thermit reaction, having product phases as inert diluents, can be written as

$$3NiO + 2Al + xAl_2O_3 \rightarrow (x + 1)\, Al_2O_3 + 3\, Ni$$

and

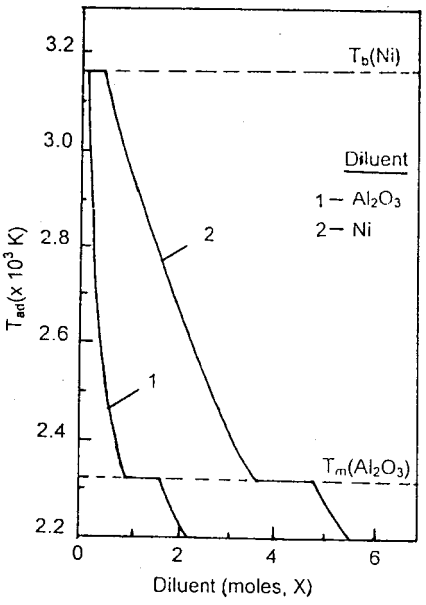

Fig. 8. Influence of dilution on the adiabatic temperature of the thermit reaction 2 in Table I.

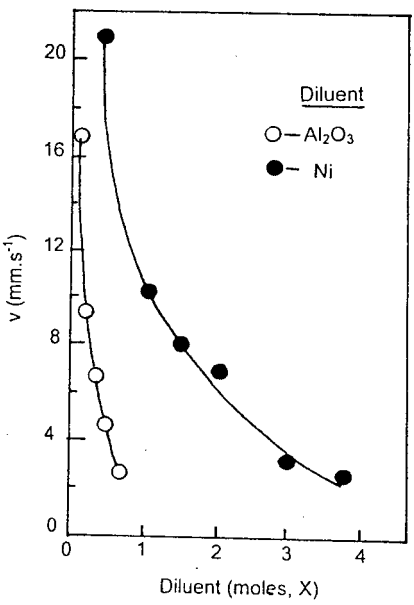

Fig. 9. Influence of dilution on the combustion velocity of the thermit reaction 2 in Table I.

$$3NiO + 2\,Al + x\,Ni \rightarrow Al_2O_3 + (x + 3)\,Ni$$

where x is the number of moles of the inert diluent added to the initial thermit mixture (ie. 3 NiO + 2Al). The adiabatic temperatures of these reactions for different values of x were determined from eqn.(1) using thermodynamic functions of heat capacities and enthalpies of formation and transformation of the product phases. Fig. 8 shows the effects of addition of Al_2O_3 and Ni diluents on T_{ad} of the thermit reaction 2. It can be seen that T_{ad} remains constant at 3183K (ie. The boiling point of Ni) upto the addition of about 0.1 moles of Al_2O_3 and 0.46 moles of Ni to the initial thermit mixture (ie. 3NiO + 2Al). This is due to the heat absorbed by the diluents from the heat generated by the thermit reaction to prevent boiling and vaporisation of Ni produced by the thermit reaction. Further increase in dilution decreases T_{ad}. When x reaches 0.9 moles of Al_2O_3 or 3.7 moles of Ni, T_{ad} reaches the melting point of Al_2O_3(ie. 2323K). The T_{ad} remains constant at 2323K till x reaches 1.7 moles of Al_2O_3 or 4.9 moles of Ni. This is due to the absorption of latent heat of melting of Al_2O_3, produced by the thermit reaction, by the diluents. Further increase in dilution causes decrease in T_{ad} further and Al_2O_3 and Ni will be in solid and liquid states respectively. Fig. 8 also shows that Al_2O_3 diluent has greater effect on T_{ad} compared to Ni diluent. This is due to the higher specific heat of Al_2O_3 compared to Ni at all temperatures[22].

The ability of the reaction 2 to self propagate and the velocity of combustion (v) during self propagation, when the reaction is diluted with Al_2O_3 or Ni diluent, were determined by static combustion experiments. In these experiments, 15mm diameter and 28mm long cylindrical compacts with green densities of about 45% of the theoretical densities of the respective mixtures, containing the required amounts of Al_2O_3 or Ni diluents, were prepared in a mechanical press. Each compact was ignited at one end using electric arc. The time taken by the combustion wave to propagate from one end to the other of each compact was noted and the velocities of combustion were determined for different values of x of Al_2O_3 and Ni. The self propagation of the diluted thermit reaction was found to stop when x is greater than 0.6 moles of Al_2O_3 or 3.7 moles of Ni. This means that these

quantities of the diluents can be added to the initial thermit mixture of the reaction and still retain the self propagating ability of the reaction so that it can be used in the methods (a) and (b) described earlier. This also shows that the thickness of the ceramic lining by method (a) and the size of the shaped casting of Ni by method (b) can be increased to these extents using the same quantity of undiluted thermit mixture of the thermit reaction 2. Fig.9 shows the effects of dilution on v of the reaction 2 when the thermit reaction is diluted with Al_2O_3 or Ni diluent. It can be seen that the addition of either of the diluents decreases v of the reaction This is due to the absorption of heat of reaction by the diluents and the longer transport distances between the reactants. The reaction also becomes less violent with the increase in dilution. Fig.9 also shows that Al_2O_3 dilution has greater effect on v compared to Ni dilution. This may be attributed to the lower thermal conductivity of Al_2O_3 compared to that of Ni[22].

2. CONCLUSIONS

Ceramic linings for metal pipes and conical parts, and shaped castings of metals and alloys have been produced by carrying out the thermit reactions under the influence of centrifugal force. The adiabatic temperature and combustion velocity of such a thermit reaction decrease with the increase in dilution when the product phases of the reaction are used as inert diluents. Beyond certain dilution, the self propagating property of the reaction gets terminated. Dilution has profound effects on combustion velocity and adiabatic temperature of the reaction when ceramic product phase of the reaction is used as the inert diluent. Dilution helps in increasing the thickness of the ceramic lining and the size of the shaped casting from metals and alloys by using the same quantity of undiluted thermit mixture.

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REFERENCES

1. Goldschmidt, H., Iron Age, 1908, **82**, 232.
2. Goldschmidt, H., and Vautin, C., J. Soc. chem. Ind., 1898, **19**, 543.
3. Mehra, O.K., Bose, D. K., and Gupta, C. K., Metall. Trans., 1973, **4**, 691.
4. Belitskus, D., J. Metals, 1972, January, 30.
5. Idem, ibid, 1973, May, 39.
6. Perfect, F. H., Trans. Metall. Soc. AIME, 1967, **239,** 1282.
7. Odawara, O., Trans. Jpn. Inst. Met., 1985, **26(8)**, 578.
8. Odawara, O., and Ikeuchi, J., J. Jpn. Inst. Met., 1981, **45**, 316.

9. Idem, J. Am. Ceram. Soc., 1986, **69(4)**, C.80-C.81.
10. Idem, Trans. Jpn. Inst. Met., 1986, **27**, 702.
11. A .G. Merzanov, V. I. Jukhvid, I. P. Borovinskaya and F. I. Dobovitsky, UK Pat.1497025 (1978).
12. Munir, Z. A., and Anselmi-Tamburini, U., Mater. Sci. Rpts., 1989, **3**, 277.
13. Walton, J. D. and Poulous, N. E., J. Amer. Ceram. Soc., 1959, **42**, 40.
14. Cutler, R. A., Virkar, A. V., and Holt, J. B., Ceram. Engg. Sci., 1985, **6**, 715.
15. Logan, K. V., and Walton, J. D., Ceram. Engg. Sci. Proc., 1984, **5**, 712.
16. Shaffer, G. B., and McCormick, P. G., Appl. Phys. Lett., 1989, **55(1)**, 45.
17. R.Seshadri, Pat. pending.
18. R.Seshadri, Pat. pending.
19. Holt, J. B., and Munir, Z. A., J. Mater. Sci., 1986, **21,** 251.
20. Munir, Z. A., Cer .Bull.,1986, **67(2)**, 342.
21. Subramanyam, J., Vijayakumar, M., and Ranganath, S., Met. Mater. and Proc., 1989, **1(2)**, 105.
22. Smithells Metals Reference Book, Sixth edn., Ed., Eric A Brandes, Butterworths, 1983